10/585992
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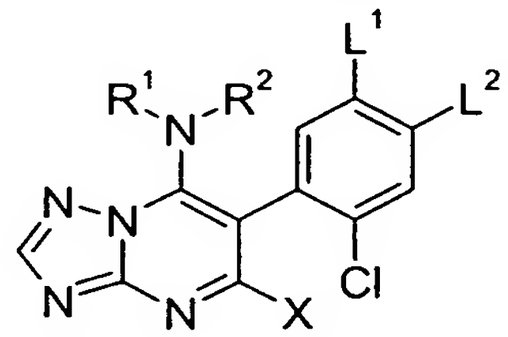
6-(2-chloro-5-halophenyl)triazolopyrimidines, their preparation and their use for controlling harmful fungi, and compositions comprising these compounds

Description

The present invention relates to substituted triazolopyrimidines of the formula I



I

in which the substituents are as defined below:

R^1, R^2 independently of one another are hydrogen, C_1-C_8-alkyl, C_1-C_8-haloalkyl, C_3-C_8-cycloalkyl, C_3-C_8-halocycloalkyl, C_2-C_8-alkenyl, C_2-C_8-haloalkenyl, C_3-C_6-cycloalkenyl, C_3-C_6-halocycloalkenyl, C_2-C_8-alkynyl, C_2-C_8-haloalkynyl or phenyl, naphthyl, or a 5- or 6-membered saturated, partially unsaturated or aromatic heterocycle which contains one to four heteroatoms from the group consisting of O, N and S,

R^1 and R^2 together with the nitrogen atom to which they are attached may also form a 5- or 6-membered heterocyclyl or heteroaryl which is attached via N and may contain 1 to 3 further heteroatoms from the group consisting of O, N and S as ring members and/or may carry one or more substituents from the group consisting of halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_2-C_6-alkenyl, C_2-C_6-haloalkenyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_3-C_6-alkenyloxy, C_3-C_6-haloalkenyloxy, C_1-C_6-alkylene and oxy-C_1-C_3-alkyleneoxy;

R^1 and/or R^2 may carry one to four identical or different groups R^a:

R^a is halogen, cyano, nitro, hydroxyl, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_1-C_6-alkylcarbonyl, C_3-C_6-cycloalkyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_1-C_6-alkoxycarbonyl, C_1-C_6-alkylthio, C_1-C_6-alkylamino, di-C_1-C_6-alkylamino, C_2-C_8-alkenyl, C_2-C_8-haloalkenyl, C_3-C_8-cycloalkenyl, C_2-C_6-alkenyloxy, C_3-C_6-haloalkenyloxy, C_2-C_6-alkynyl, C_2-C_6-haloalkynyl, C_3-C_6-alkynyloxy, C_3-C_6-haloalkynyloxy, C_3-C_6-cycloalkoxy, C_3-C_6-cycloalkenyloxy, oxy-C_1-C_3-alkyleneoxy, phenyl, naphthyl, a 5- to 10-membered saturated, partially unsaturated or aromatic heterocycle which

contains one to four heteroatoms from the group consisting of O, N and S,

where these aliphatic, alicylic or aromatic groups for their part may be partially or fully halogenated or may carry one to three groups R^b:

R^b is halogen, cyano, nitro, hydroxyl, mercapto, amino, carboxyl, aminocarbonyl, aminothiocarbonyl, alkyl, haloalkyl, alkenyl, alkenyloxy, alkynyloxy, alkoxy, haloalkoxy, alkylthio, alkylamino, dialkylamino, formyl, alkylcarbonyl, alkylsulfonyl, alkylsulfoxyl, alkoxycarbonyl, alkylcarbonyloxy, alkylaminocarbonyl, dialkylaminocarbonyl, alkylaminothiocarbonyl, dialkylaminothiocarbonyl, where the alkyl groups in these radicals contain 1 to 6 carbon atoms and the alkenyl or alkynyl groups mentioned in these radicals contain 2 to 8 carbon atoms;

and/or one to three of the following radicals:

cycloalkyl, cycloalkoxy, heterocyclyl, heterocyclyloxy, where the cyclic systems contain 3 to 10 ring members; aryl, aryloxy, arylthio, aryl-C_1-C_6-alkoxy, aryl-C_1-C_6-alkyl, hetaryl, hetaryloxy, hetarylthio, where the aryl radicals preferably contain 6 to 10 ring members and the hetaryl radicals 5 or 6 ring members, where the cyclic systems may be partially or fully halogenated or substituted by alkyl or haloalkyl groups;

L^1 is fluorine, chlorine or bromine, and

L^2 is hydrogen, C_1-C_4-alkyl or C_1-C_4-alkoxy; and

X is halogen, cyano, C_1-C_4-alkyl, C_1-C_4-haloalkyl, C_1-C_4-alkoxy or C_1-C_2-haloalkoxy.

Moreover, the invention relates to processes and intermediates for preparing these compounds, to compositions comprising them and to their use for controlling phytopathogenic harmful fungi.

5-chloro-6-phenyl-7-aminotriazolopyrimidines are known in a general manner from EP-A 71 792 and EP-A 550 113. 6-(2-Cl-phenyl)-7-amino-triazolopyrimidines whose 6-

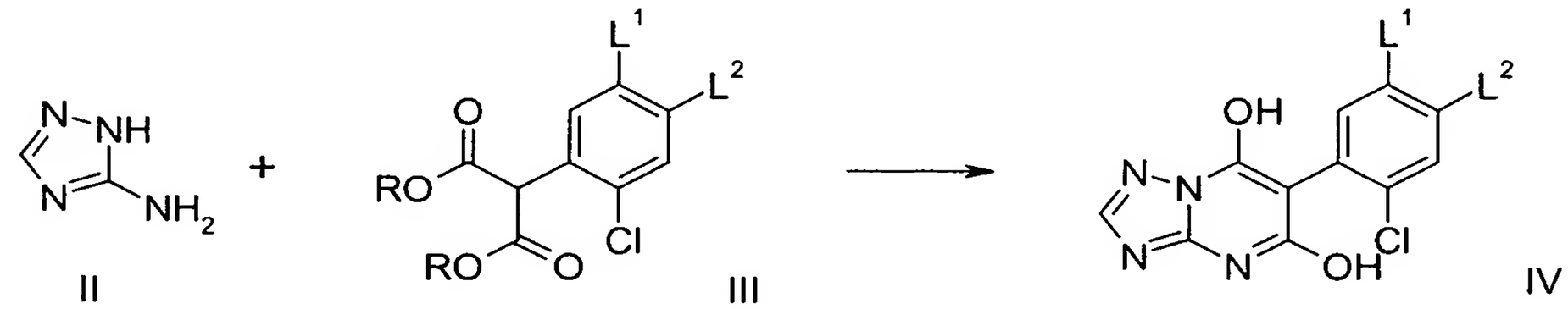
phenyl group is further substituted by halogen are proposed in a general manner in EP-A 550 113, FR-A 27 84 991, US 5 994 360, WO 98/46608, JP-A 2002/308 879, WO 02/38565, WO 02/083677, WO 02/088125, WO 02/088126 and WO 02/088127. Triazolopyrimidines where the 6-phenyl group is substituted by 4-alkyl or 4-alkoxyl, are known from WO 98/48893, WO 03/008417 and WO 03/093271. These compounds are known to be suitable for controlling harmful fungi.

The compounds according to the invention differ from those described in the publications mentioned above by the 2,5-disubstitution of the 6-phenyl ring.

In many cases, the activity of the known compounds is unsatisfactory. Based on this, it is an object of the present invention to provide compounds having improved activity and/or a broader activity spectrum.

Accordingly, the compounds defined at the outset have been found. Moreover, processes and intermediates for their preparation, compositions comprising them and methods for controlling harmful fungi using the compounds I have been found.

The compounds according to the invention can be obtained by different routes. Advantageously, they are prepared by reaction of 5-aminotriazole of the formula II with appropriately substituted phenylmalonates of the formula III in which R is alkyl, preferably C_1-C_6-alkyl, in particular methyl or ethyl.



This reaction is usually carried out at temperatures of from 80°C to 250°C, preferably from 120°C to 180°C, without solvent or in an inert organic solvent in the presence of a base [cf. EP-A 770 615] or in the presence of acetic acid under the conditions known from Adv. Het. Chem. 57 (1993), 81 ff.

Suitable solvents are aliphatic hydrocarbons, aromatic hydrocarbons, such as toluene, o-, m- and p-xylene, halogenated hydrocarbons, ethers, nitriles, ketones, alcohols, and also N-methylpyrrolidone, dimethyl sulfoxide, dimethylformamide and dimethylacetamide. With particular preference, the reaction is carried out in the

absence of solvent or in chlorobenzene, xylene, dimethyl sulfoxide or N-methyl-pyrrolidone. It is also possible to use mixtures of the solvents mentioned.

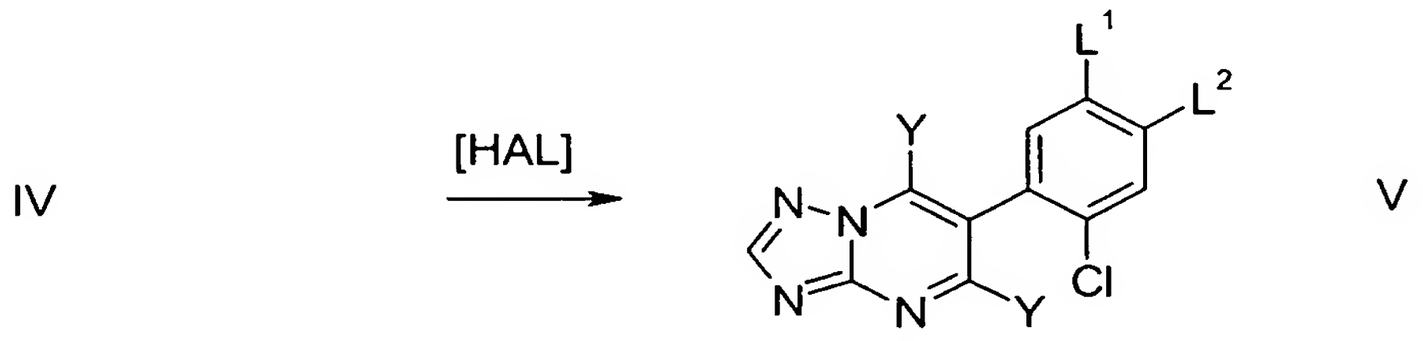
Suitable bases are, in general, inorganic compounds, such as alkali metal and alkaline earth metal hydroxides, alkali metal and alkaline earth metal oxides, alkali metal and alkaline earth metal hydrides, alkali metal amides, alkali metal and alkaline earth metal carbonates, and also alkali metal bicarbonates, organometallic compounds, in particular alkali metal alkyls, alkyl magnesium halides and also alkali metal and alkaline earth metal alkoxides and dimethoxymagnesium, moreover organic bases, for example tertiary amines, such as trimethylamine, triethylamine, triisopropylethylamine, tributylamine and N-methylpiperidine, N-methylmorpholine, pyridine, substituted pyridines, such as collidine, lutidine and 4-dimethylaminopyridine, and also bicyclic amines. Particular preference is given to using tertiary amines, such as triisopropylethylamine, tributylamine, N-methylmorpholine or N-methylpiperidine.

The bases are generally employed in catalytic amounts; however, they can also be employed in equimolar amounts, in excess or, if appropriate, as solvent.

The starting materials are generally reacted with one another in equimolar amounts. In terms of yield, it may be advantageous to use an excess of the base and the malonate III, based on the triazole.

Phenylmalonates of the formula III are advantageously obtained from the reaction of appropriately substituted bromobenzenes with dialkyl malonates under Cu(I) catalysis [cf. Chemistry Letters (1981), 367-370; EP-A 10 02 788].

The dihydroxytriazolopyrimidines of the formula IV are converted under the conditions known from WO-A 94/20501 into the dihalopyrimidines of the formula V in which y is a halogen atom, preferably a bromine or a chlorine atom, in particular a chlorine atom. The halogenating agent [HAL] used is advantageously a chlorinating agent or a brominating agent, such as phosphorus oxybromide or phosphorus oxychloride, if appropriate in the presence of a solvent.



This reaction is usually carried out at from 0°C to 150°C, preferably from 80°C to 125°C [cf. EP-A 770 615].

Dihalopyrimidines of the formula V are reacted further with amines of the formula VI

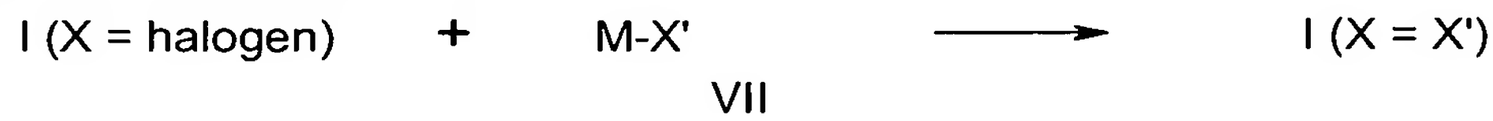
VI

in which R^1 and R^2 are as defined in formula I, to give compounds of the formula I in which X is halogen.

This reaction is advantageously carried out at from 0°C to 70°C, preferably from 10°C to 35°C, preferably in the presence of an inert solvent, such as an ether, for example dioxane, diethyl ether or, in particular, tetrahydrofuran, a halogenated hydrocarbon, such as dichloromethane, or an aromatic hydrocarbon, such as, for example, toluene [cf. WO-A 98/46608].

Preference is given to using a base, such as a tertiary amine, for example triethylamine, or an inorganic amine, such as potassium carbonate; it is also possible for excess amine of the formula VI to serve as base.

Compounds of the formula I in which X is cyano, C_1-C_6-alkoxy or C_1-C_2-haloalkoxy can be obtained in an advantageous manner by reacting compounds I in which X is halogen, preferably chlorine, with compounds M-X' (formula VII). Depending on the meaning of the group X' to be introduced, the compounds VII are inorganic cyanides, alkoxylates or haloalkoxylates. The reaction is advantageously carried out in the presence of an inert solvent. The cation M in formula VII is of little importance; for practical reasons, ammonium, tetraalkylammonium or alkali metal or alkaline earth metal salts are usually preferred.

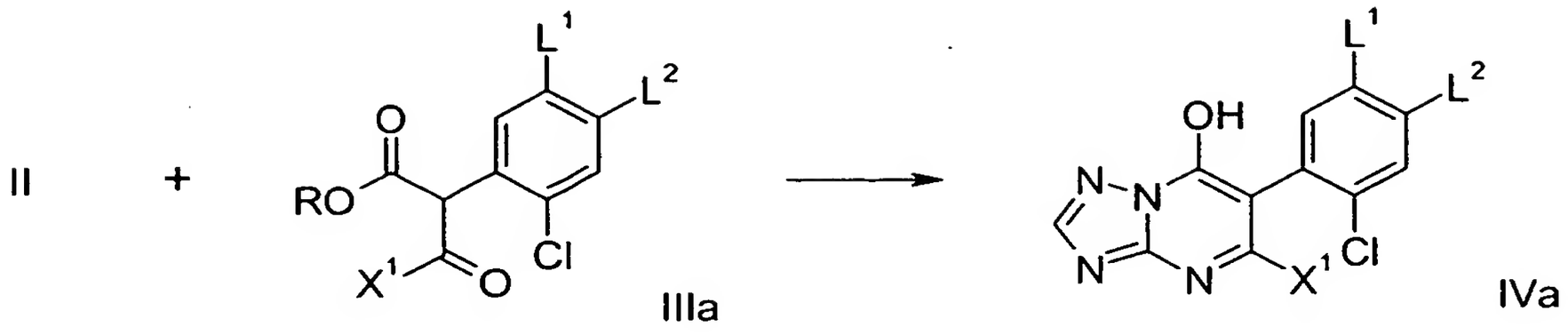


VII

The reaction temperature is usually from 0 to 120°C, preferably from 10 to 40°C [cf. J. Heterocycl. Chem. 12 (1975), 861-863].

Suitable solvents include ethers, such as dioxane, diethyl ether and, preferably, tetrahydrofuran, alchohols, such as methanol or ethanol, halogenated hydrocarbons, such as dichloromethane, and aromatic hydrocarbons, such as toluene, or acetonitrile.

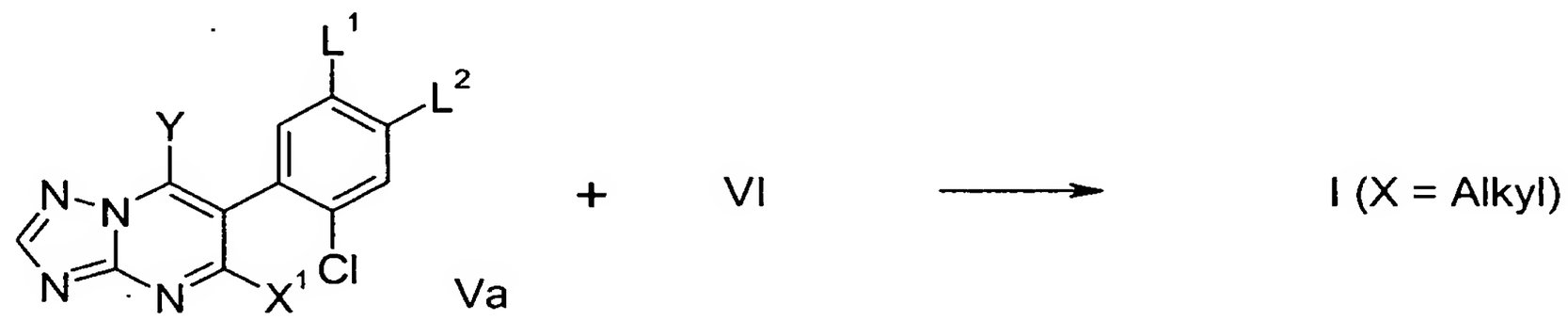
Compounds of the formula I, in which X is C_1-C_4-alkyl or C_1–C_4–haloalkyl can be obtained in an advantageous manner by the following synthesis route:



II + IIIa → IVa

Starting with the keto esters IIIa, 5-alkyl-7-hydroxy-6-phenyltriazolopyrimidines IVa are obtained. In the formulae IIIa and IVa, X^1 is C_1-C_4-alkyl or C_1–C_4–haloalkyl. By using the easily obtainable 2-phenylacetoacetates (IIIa where $X^1 = CH_3$), the 5-methyl-7-hydroxy-6-phenyltriazolopyrimidines are obtained [cf. Chem. Pharm. Bull., 9 (1961), 801]. The starting materials IIIa are advantageously prepared under the conditions described in EP-A 10 02 788.

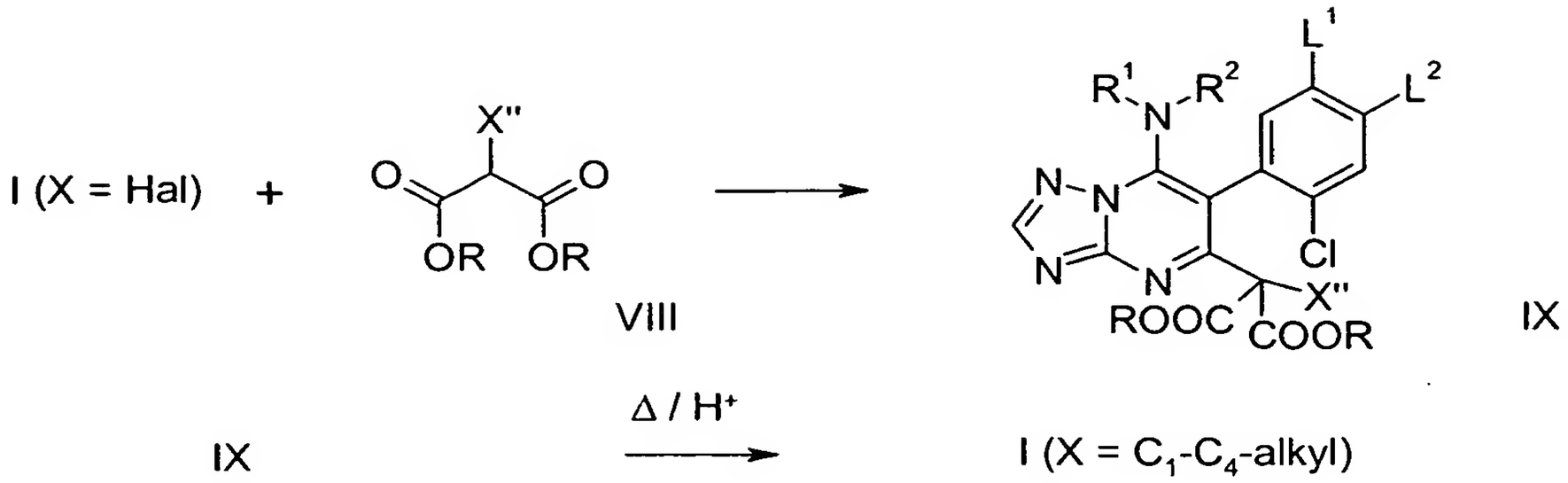
The resulting 5-alkyl-7-hydroxy-6-phenyltriazolopyrimidines are reacted with halogenating agents [HAL] under the conditions described further above to give the 7-halotriazolopyrimidines of the formula Va in which y is a halogen atom. Preference is given to using chlorinating or brominating agents such as phosphorus oxybromide, phosphorus oxychloride, thionyl chloride, thionyl bromide or sulfuryl chloride. The reaction can be carried out neat or in the presence of a solvent. Customary reaction temperatures are from 0 to 150°C or, preferably, from 80 to 125°C.



Va + VI → I (X = Alkyl)

The reaction of Va with amines VI is carried out under the conditions described further above.

Alternatively, compounds of the formula I in which X is C_1-C_4-alkyl can also be prepared from compounds I in which X is halogen, in particular chlorine, and malonates of the formula VIII. In formula VIII, X" is hydrogen or C_1-C_3-alkyl and R is C_1-C_4-alkyl. They are reacted to give compounds of the formula IX and decarboxylated to give compounds I [cf. US 5,994,360].



The malonates VIII are known from the literature [J. Am. Chem. Soc., 64 (1942), 2714; J. Org. Chem., 39 (1974), 2172; Helv. Chim. Acta, 61 (1978), 1565], or they can be prepared in accordance with the literature cited.

The subsequent hydrolysis of the ester IX is carried out under generally customary conditions; depending on the various structural elements, alkaline or acidic hydrolysis of the compounds IX may be advantageous. Under the conditions of the ester hydrolysis, there may be complete or partial decarboxylation to I.

The decarboxylation is usually carried out at temperatures of from 20°C to 180°C, preferably from 50°C to 120°C, in an inert solvent, if appropriate in the presence of an acid.

Suitable acids are hydrochloric acid, sulfuric acid, phosphoric acid, formic acid, acetic acid, p-toluenesulfonic acid. Suitable solvents are water, aliphatic hydrocarbons, such as pentane, hexane, cyclohexane and petroleum ether, aromatic hydrocarbons, such as toluene, o-, m- and p-xylene, halogenated hydrocarbons, such as methylene chloride, chloroform and chlorobenzene, ethers, such as diethyl ether, diisopropyl ether, tert-butyl methyl ether, dioxane, anisole and tetrahydrofuran, nitriles, such as acetonitrile and propionitrile, ketones, such as acetone, methyl ethyl ketone, diethyl ketone and tert-butyl methyl ketone, alcohols, such as methanol, ethanol, n-propanol, isopropanol, n-butanol and tert-butanol, and also dimethyl sulfoxide, dimethylformamide and dimethyl acetamide; particularly preferably, the reaction is carried out in hydrochloric acid or acetic acid. It is also possible to use mixtures of the solvents mentioned.

Compounds of the formula I in which X is C_1-C_4-alkyl can also be obtained by coupling 5-halotriazolopyrimidines of the formula I in which X is halogen with organometallic

reagents of the formula X. In one embodiment of this process, the reaction is carried out with transition metal catalysis, such as Ni or Pd catalysis.

X

In formula X, M is a metal ion of the valency y, such as, for example, B, Zn or Sn, and X" is C_1-C_3-alkyl. This reaction can be carried out, for example, analogously to the following methods: J. Chem. Soc. Perkin Trans. 1, (1994), 1187, ibid 1 (1996), 2345; WO-A 99/41255; Aust. J. Chem. 43 (1990), 733; J. Org. Chem. 43 (1978), 358; J. Chem. Soc. Chem. Commun. (1979), 866; Tetrahedron Lett. 34 (1993), 8267; ibid 33 (1992), 413.

The reaction mixtures are worked up in a customary manner, for example by mixing with water, separating the phases and, if appropriate, chromatographic purification of the crude products. Some of the intermediates and end products are obtained in the form of colorless or slightly brownish viscous oils which are purified or freed from volatile components under reduced pressure and at moderately elevated temperature. If the intermediates and end products are obtained as solids, purification can also be carried out by recrystallization or digestion.

If individual compounds I cannot be obtained by the routes described above, they can be prepared by derivatization of other compounds I.

If the synthesis yields mixtures of isomers, a separation is generally not necessarily required however since in some cases the individual isomers can be interconverted during work-up for use or during use (for example under the action of light, acids or bases). Such conversions may also take place after use, for example in the treatment of plants in the treated plant, or in the harmful fungus to be controlled.

In the definitions of the symbols given in the formulae above, collective terms were used which are generally representative of the following substituents:

halogen: fluorine, chlorine, bromine and iodine;

alkyl: saturated straight-chain or branched hydrocarbon radicals having 1 to 4, 6 or 8 carbon atoms, for example C_1-C_6-alkyl, such as methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 2-methylpropyl, 1,1-dimethylethyl, pentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 2,2-dimethylpropyl, 1-ethylpropyl, hexyl, 1,1-dimethylpropyl, 1,2-dimethylpropyl, 1-methylpentyl, 2-methylpentyl, 3-methylpentyl, 4-methylpentyl, 1,1-dimethylbutyl, 1,2-dimethylbutyl, 1,3-dimethylbutyl, 2,2-dimethylbutyl, 2,3-

dimethylbutyl, 3,3-dimethylbutyl, 1-ethylbutyl, 2-ethylbutyl, 1,1,2-trimethylpropyl, 1,2,2-trimethylpropyl, 1-ethyl-1-methylpropyl and 1-ethyl-2-methylpropyl;

haloalkyl: straight-chain or branched alkyl groups having 1 to 2, 4 or 6 carbon atoms (as mentioned above), where in these groups some or all of the hydrogen atoms may be replaced by halogen atoms as mentioned above: in particular, C_1-C_2-haloalkyl, such as chloromethyl, bromomethyl, dichloromethyl, trichloromethyl, fluoromethyl, difluoromethyl, trifluoromethyl, chlorofluoromethyl, dichlorofluoromethyl, chlorodifluoromethyl, 1-chloroethyl, 1-bromoethyl, 1-fluoroethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2,2,2-trifluoroethyl, 2-chloro-2-fluoroethyl, 2-chloro-2,2-difluoroethyl, 2,2-dichloro-2-fluoroethyl, 2,2,2-trichloroethyl, pentafluoroethyl or 1,1,1-trifluoroprop-2-yl;

alkenyl: unsaturated straight-chain or branched hydrocarbon radicals having 2 to 4, 6 or 8 carbon atoms and one or two double bonds in any position, for example C_2-C_6-alkenyl, such as ethenyl, 1-propenyl, 2-propenyl, 1-methylethenyl, 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 2-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-2-propenyl, 1-pentenyl, 2-pentenyl, 3-pentenyl, 4-pentenyl, 1-methyl-1-butenyl, 2-methyl-1-butenyl, 3-methyl-1-butenyl, 1-methyl-2-butenyl, 2-methyl-2-butenyl, 3-methyl-2-butenyl, 1-methyl-3-butenyl, 2-methyl-3-butenyl, 3-methyl-3-butenyl, 1,1-dimethyl-2-propenyl, 1,2-dimethyl-1-propenyl, 1,2-dimethyl-2-propenyl, 1-ethyl-1-propenyl, 1-ethyl-2-propenyl, 1-hexenyl, 2-hexenyl, 3-hexenyl, 4-hexenyl, 5-hexenyl, 1-methyl-1-pentenyl, 2-methyl-1-pentenyl, 3-methyl-1-pentenyl, 4-methyl-1-pentenyl, 1-methyl-2-pentenyl, 2-methyl-2-pentenyl, 3-methyl-2-pentenyl, 4-methyl-2-pentenyl, 1-methyl-3-pentenyl, 2-methyl-3-pentenyl, 3-methyl-3-pentenyl, 4-methyl-3-pentenyl, 1-methyl-4-pentenyl, 2-methyl-4-pentenyl, 3-methyl-4-pentenyl, 4-methyl-4-pentenyl, 1,1-dimethyl-2-butenyl, 1,1-dimethyl-3-butenyl, 1,2-dimethyl-1-butenyl, 1,2-dimethyl-2-butenyl, 1,2-dimethyl-3-butenyl, 1,3-dimethyl-1-butenyl, 1,3-dimethyl-2-butenyl, 1,3-dimethyl-3-butenyl, 2,2-dimethyl-3-butenyl, 2,3-dimethyl-1-butenyl, 2,3-dimethyl-2-butenyl, 2,3-dimethyl-3-butenyl, 3,3-dimethyl-1-butenyl, 3,3-dimethyl-2-butenyl, 1-ethyl-1-butenyl, 1-ethyl-2-butenyl, 1-ethyl-3-butenyl, 2-ethyl-1-butenyl, 2-ethyl-2-butenyl, 2-ethyl-3-butenyl, 1,1,2-trimethyl-2-propenyl, 1-ethyl-1-methyl-2-propenyl, 1-ethyl-2-methyl-1-propenyl and 1-ethyl-2-methyl-2-propenyl;

haloalkenyl: unsaturated straight-chain or branched hydrocarbon radicals having 2 to 8 carbon atoms and one or two double bonds in any position (as mentioned above), where in these groups some or all of the hydrogen atoms may be replaced by halogen atoms as mentioned above, in particular by fluorine, chlorine and bromine;

alkynyl: straight-chain or branched hydrocarbon groups having 2 to 4, 6 or 8 carbon atoms and one or two triple bonds in any position, for example C_2-C_6-alkynyl, such as ethynyl, 1-propynyl, 2-propynyl, 1-butynyl, 2-butynyl, 3-butynyl, 1-methyl-2-propynyl, 1-pentynyl, 2-pentynyl, 3-pentynyl, 4-pentynyl, 1-methyl-2-butynyl, 1-methyl-3-butynyl, 2-methyl-3-butynyl, 3-methyl-1-butynyl, 1,1-dimethyl-2-propynyl, 1-ethyl-2-propynyl, 1-hexynyl, 2-hexynyl, 3-hexynyl, 4-hexynyl, 5-hexynyl, 1-methyl-2-pentynyl, 1-methyl-3-pentynyl, 1-methyl-4-pentynyl, 2-methyl-3-pentynyl, 2-methyl-4-pentynyl, 3-methyl-1-pentynyl, 3-methyl-4-pentynyl, 4-methyl-1-pentynyl, 4-methyl-2-pentynyl, 1,1-dimethyl-2-butynyl, 1,1-dimethyl-3-butynyl, 1,2-dimethyl-3-butynyl, 2,2-dimethyl-3-butynyl, 3,3-dimethyl-1-butynyl, 1-ethyl-2-butynyl, 1-ethyl-3-butynyl, 2-ethyl-3-butynyl and 1-ethyl-1-methyl-2-propynyl;

cycloalkyl: mono- or bicyclic saturated hydrocarbon groups having 3 to 6 or 8 carbon ring members, for example C_3-C_8-cycloalkyl such as cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl;

five- to ten-membered saturated, partially unsaturated or aromatic heterocycle which contains one to four heteroatoms from the group consisting of O, N and S:

- 5- or 6-membered heterocyclyl which contains one to three nitrogen atoms and/or one oxygen or sulfur atom or one or two oxygen and/or sulfur atoms, for example 2-tetrahydrofuranyl, 3-tetrahydrofuranyl, 2-tetrahydrothienyl, 3-tetrahydrothienyl, 2-pyrrolidinyl, 3-pyrrolidinyl, 3-isoxazolidinyl, 4-isoxazolidinyl, 5-isoxazolidinyl, 3-isothiazolidinyl, 4-isothiazolidinyl, 5-isothiazolidinyl, 3-pyrazolidinyl, 4-pyrazolidinyl, 5-pyrazolidinyl, 2-oxazolidinyl, 4-oxazolidinyl, 5-oxazolidinyl, 2-thiazolidinyl, 4-thiazolidinyl, 5-thiazolidinyl, 2-imidazolidinyl, 4-imidazolidinyl, 2-pyrrolin-2-yl, 2-pyrrolin-3-yl, 3-pyrrolin-2-yl, 3-pyrrolin-3-yl, 2-piperidinyl, 3-piperidinyl, 4-piperidinyl, 1,3-dioxan-5-yl, 2-tetrahydropyranyl, 4-tetrahydropyranyl, 2-tetrahydrothienyl, 3-hexahydropyridazinyl, 4-hexahydropyridazinyl, 2-hexahydropyrimidinyl, 4-hexahydropyrimidinyl, 5-hexahydropyrimidinyl and 2-piperazinyl;

- 5-membered heteroaryl which contains one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom: 5-membered heteroaryl groups which, in addition to carbon atoms, may contain one to four nitrogen atoms or one to three nitrogen atoms and one sulfur or oxygen atom as ring members, for example 2-furyl, 3-furyl, 2-thienyl, 3-thienyl, 2-pyrrolyl, 3-pyrrolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-imidazolyl, 4-imidazolyl and 1,3,4-triazol-2-yl;

- 6-membered heteroaryl which contains one to three or one to four nitrogen atoms: 6-membered heteroaryl groups which, in addition to carbon atoms, may contain one to three or one to four nitrogen atoms as ring members, for example 2-pyridinyl, 3-pyridinyl, 4-pyridinyl, 3-pyridazinyl, 4-pyridazinyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl and 2-pyrazinyl;

alkylene: divalent unbranched chains of 3 to 5 CH_2 groups, for example CH_2, CH_2CH_2, $CH_2CH_2CH_2$, $CH_2CH_2CH_2CH_2$ and $CH_2CH_2CH_2CH_2CH_2$;

oxyalkylene: divalent unbranched chains of 2 to 4 CH_2 groups, where one valency is attached to the skeleton via an oxygen atom, for example OCH_2CH_2, $OCH_2CH_2CH_2$ and $OCH_2CH_2CH_2CH_2$;

oxyalkylenoxy: divalent unbranched chains of 1 to 3 CH_2 groups, where both valencies are attached to the skeleton via an oxygen atom, for example OCH_2O, OCH_2CH_2O and $OCH_2CH_2CH_2O$.

The scope of the present invention includes the (R)- and (S)-isomers and the racemates of compounds of the formula I having chiral centers.

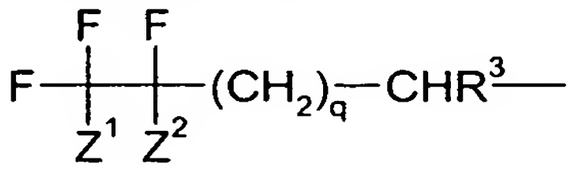
The particularly preferred embodiments of the intermediates with respect to the variables correspond to those of groups L of the formula I.

With a view to the intended use of the triazolopyrimidines of the formula I, particular preference is given to the following meanings of the substituents, in each case on their own or in combination:

Preference is given to compounds of the formula I in which R^1 is not hydrogen.

Particular preference is given to compounds I in which R^1 is C_1-C_6-alkyl, C_2-C_6-alkenyl, C_2-C_6-alkynyl or C_1-C_8-haloalkyl.

Preference is given to compounds I in which R^1 is a group A:



A

in which

Z^1 is hydrogen, fluorine or C_1-C_6-fluoroalkyl,

Z^2 is hydrogen or fluorine, or

Z^1 and Z^2 together form a double bond;

q is 0 or 1; and

R^3 is hydrogen or methyl.

Moreover, preference is given to compounds I in which R^1 is C_3-C_6-cycloalkyl which may be substituted by C_1-C_4-alkyl.

Particular preference is given to compounds I in which R^2 is hydrogen.

Preference is likewise given to compounds I in which R^2 is methyl or ethyl.

If R^1 and/or R^2 comprise haloalkyl or haloalkenyl groups having a center of chirality, the (S) isomers are preferred for these groups. In the case of halogen-free alkyl or alkenyl groups having a center of chirality in R^1 or R^2, preference is given to the (R)-configured isomers.

Preference is furthermore given to compounds I in which R^1 and R^2 together with the nitrogen atom to which they are attached form a piperidinyl, morpholinyl or thiomorpholinyl ring, in particular a piperidinyl ring, which, if appropriate, is substituted by one to three groups halogen, C_1-C_4-alkyl or C_1-C_4-haloalkyl. Particular preference is given to the compounds in which R^1 and R^2 together with the nitrogen atom to which they are attached form a 4-methylpiperidine ring.

The invention furthermore preferably provides compounds I in which R^1 and R^2 together with the nitrogen atom to which they are attached form a pyrazole ring which, if appropriate, is substituted by one or two groups halogen, C_1-C_4-alkyl or C_1-C_4-haloalkyl, in particular by 3,5-dimethyl or 3,5-di(trifluoromethyl).

In addition, particular preference is also given to compounds of the formula I in which R^1 is $CH(CH_3)$-CH_2CH_3, $CH(CH_3)$-$CH(CH_3)_2$, $CH(CH_3)$-$C(CH_3)_3$, $CH(CH_3)$-CF_3, $CH_2C(CH_3)=CH_2$, $CH_2CH=CH_2$, cyclopentyl or cyclohexyl; R^2 is hydrogen or methyl; or R^1 and R^2 together are $-(CH_2)_2CH(CH_3)(CH_2)_2-$, $-(CH_2)_2CH(CF_3)(CH_2)_2-$ or $-(CH_2)_2O(CH_2)_2-$.

Preference is given to compounds I in which X is halogen, C_1-C_4-alkyl, cyano or C_1-C_4-alkoxy, such as chlorine, methyl, cyano, methoxy or ethoxy, especially chlorine or methyl, in particular chlorine.

The present invention preferably provides compounds I in which L^1 is chlorine.

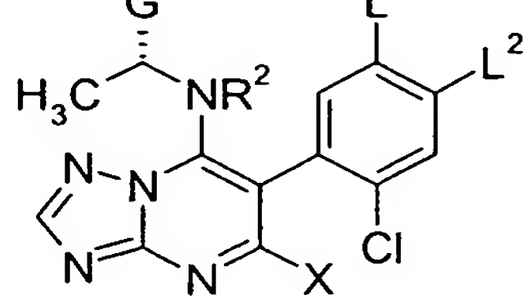
The present invention furthermore preferably provides compounds I in which L^1 is fluorine.

In another embodiment of the present invention L^1 is bromine.

The present invention particularly preferably provides compounds I in which L^2 is hydrogen.

In another embodiment of the present invention, L^2 is methyl or methoxy.

A preferred embodiment of the invention relates to compounds of the formula I.1:



I.1

in which

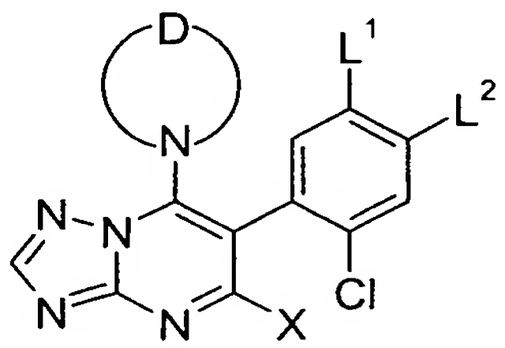
G is C_2-C_6-alkyl, in particular ethyl, n- and isopropyl, n-, sec-, tert-butyl, and C_1-C_4-alkoxymethyl, in particular ethoxymethyl, or C_3-C_6-cycloalkyl, in particular cyclopentyl or cyclohexyl;

R^2 is hydrogen or methyl;

X is chlorine, methyl, cyano, methoxy or ethoxy and

L^1 and L^2 are as defined for formula I.

A further preferred embodiment of the invention relates to compounds in which R^1 and R^2 together with the nitrogen atom to which they are attached form a five- or six-membered heterocyclyl or heteroaryl which is attached via N and may contain a further heteroatom from the group consisting of O, N and S as ring member and/or may carry one or more substituents from the group consisting of halogen, C_1-C_6-alkyl, C_1-C_6-haloalkyl, C_2-C_6-alkenyl, C_2-C_6-haloalkenyl, C_1-C_6-alkoxy, C_1-C_6-haloalkoxy, C_3-C_6-alkenyloxy, C_3-C_6-haloalkenyloxy, C_1-C_6-alkylene and oxy-C_1-C_3-alkylenoxy. These compounds correspond in particular to formula I.2,



I.2

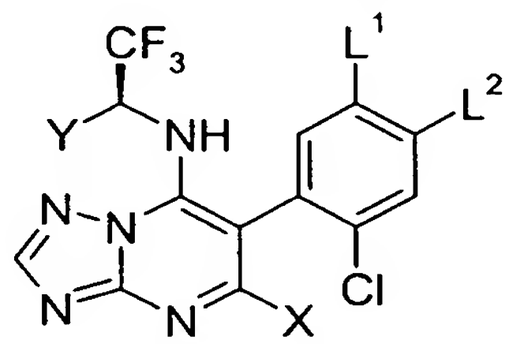
in which

D together with the nitrogen atom forms a five- or six-membered heterocyclyl or heteroaryl which is attached via N and may contain a further heteroatom from the group consisting of O, N and S as ring member and/or may carry one or more substituents from the group consisting of halogen, C_1-C_4-alkyl, C_1-C_4-alkoxy and C_1-C_2-haloalkyl; and

X is chlorine, methyl, cyano, methoxy or ethoxy and

L^1 and L^2 are as defined for formula I.

A further preferred embodiment of the invention relates to compounds of the formula I.3



I.3

in which Y is hydrogen or C_1-C_4-alkyl, in particular methyl and ethyl, and X is chlorine, methyl, cyano, methoxy or ethoxy and L^1 and L^2 are as defined for formula I.

A further preferred embodiment of the invention relates to compounds in which L^1 is fluorine and L^2 is alkyl or alkoxy, in particular methyl or methoxy.

A further preferred embodiment of the invention relates to compounds in which L^1 is chlorine and L^2 is alkyl or alkoxy, in particular methyl or methoxy.

In particular with a view to their use, preference is given to the compounds I compiled in the tables below. Moreover, the groups mentioned for a substituent in the tables are per se, independently of the combination in which they are mentioned, a particularly preferred embodiment of the substituent in question.

Table 1

Compounds of the formula I in which X is chlorine, L^1 is chlorine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 2

Compounds of the formula I in which X is cyano, L^1 is chlorine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 3

Compounds of the formula I in which X is methyl, L^1 is chlorine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 4
Compounds of the formula I in which X is methoxy, L^1 is chlorine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 5
Compounds of the formula I in which X is chlorine, L^1 is fluorine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 6
Compounds of the formula I in which X is cyano, L^1 is fluorine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 7
Compounds of the formula I in which X is methyl, L^1 is fluorine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 8
Compounds of the formula I in which X is methoxy, L^1 is fluorine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 9
Compounds of the formula I in which X is chlorine, L^1 is bromine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 10
Compounds of the formula I in which X is cyano, L^1 is bromine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 11
Compounds of the formula I in which X is methyl, L^1 is bromine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 12
Compounds of the formula I in which X is methoxy, L^1 is bromine, L^2 is hydrogen and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 13
Compounds of the formula I in which X is chlorine, L^1 is chlorine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 14
Compounds of the formula I in which X is cyano, L^1 is chlorine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 15
Compounds of the formula I in which X is methyl, L^1 is chlorine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 16
Compounds of the formula I in which X is methoxy, L^1 is chlorine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 17
Compounds of the formula I in which X is chlorine, L^1 is fluorine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 18
Compounds of the formula I in which X is cyano, L^1 is fluorine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 19
Compounds of the formula I in which X is methyl, L^1 is fluorine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 20
Compounds of the formula I in which X is methoxy, L^1 is fluorine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 21
Compounds of the formula I in which X is chlorine, L^1 is bromine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 22
Compounds of the formula I in which X is cyano, L^1 is bromine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 23
Compounds of the formula I in which X is methyl, L^1 is bromine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 24
Compounds of the formula I in which X is methoxy, L^1 is bromine, L^2 is methyl and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 25
Compounds of the formula I in which X is chlorine, L^1 is chlorine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 26
Compounds of the formula I in which X is cyano, L^1 is chlorine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 27
Compounds of the formula I in which X is methyl, L^1 is chlorine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 28
Compounds of the formula I in which X is methoxy, L^1 is chlorine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 29
Compounds of the formula I in which X is chlorine, L^1 is fluorine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 30
Compounds of the formula I in which X is cyano, L^1 is fluorine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 31
Compounds of the formula I in which X is methyl, L^1 is fluorine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 32
Compounds of the formula I in which X is methoxy, L^1 is fluorine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 33
Compounds of the formula I in which X is chlorine, L^1 is bromine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 34
Compounds of the formula I in which X is cyano, L^1 is bromine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 35
Compounds of the formula I in which X is methyl, L^1 is bromine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table 36
Compounds of the formula I in which X is methoxy, L^1 is bromine, L^2 is methoxy and the combination of R^1 and R^2 corresponds for each compound to one row of table A

Table A

No.	R^1	R^2
A-1	H	H
A-2	CH_3	H
A-3	CH_3	CH_3
A-4	CH_2CH_3	H
A-5	CH_2CH_3	CH_3
A-6	CH_2CH_3	CH_2CH_3
A-7	CH_2CF_3	H
A-8	CH_2CF_3	CH_3
A-9	CH_2CF_3	CH_2CH_3
A-10	CH_2CCl_3	H
A-11	CH_2CCl_3	CH_3
A-12	CH_2CCl_3	CH_2CH_3
A-13	$CH_2CH_2CH_3$	H
A-14	$CH_2CH_2CH_3$	CH_3
A-15	$CH_2CH_2CH_3$	CH_2CH_3
A-16	$CH_2CH_2CH_3$	$CH_2CH_2CH_3$
A-17	$CH(CH_3)_2$	H
A-18	$CH(CH_3)_2$	CH_3
A-19	$CH(CH_3)_2$	CH_2CH_3
A-20	$CH_2CH_2CH_2CH_3$	H

No.	R^1	R^2
A-21	$CH_2CH_2CH_2CH_3$	CH_3
A-22	$CH_2CH_2CH_2CH_3$	CH_2CH_3
A-23	$CH_2CH_2CH_2CH_3$	$CH_2CH_2CH_3$
A-24	$CH_2CH_2CH_2CH_3$	$CH_2CH_2CH_2CH_3$
A-25	(±) $CH(CH_3)$-CH_2CH_3	H
A-26	(±) $CH(CH_3)$-CH_2CH_3	CH_3
A-27	(±) $CH(CH_3)$-CH_2CH_3	CH_2CH_3
A-28	(S) $CH(CH_3)$-CH_2CH_3	H
A-29	(S) $CH(CH_3)$-CH_2CH_3	CH_3
A-30	(S) $CH(CH_3)$-CH_2CH_3	CH_2CH_3
A-31	(R) $CH(CH_3)$-CH_2CH_3	H
A-32	(R) $CH(CH_3)$-CH_2CH_3	CH_3
A-33	(R) $CH(CH_3)$-CH_2CH_3	CH_2CH_3
A-34	(±) $CH(CH_3)$-$CH(CH_3)_2$	H
A-35	(±) $CH(CH_3)$-$CH(CH_3)_2$	CH_3
A-36	(±) $CH(CH_3)$-$CH(CH_3)_2$	CH_2CH_3
A-37	(S) $CH(CH_3)$-$CH(CH_3)_2$	H
A-38	(S) $CH(CH_3)$-$CH(CH_3)_2$	CH_3
A-39	(S) $CH(CH_3)$-$CH(CH_3)_2$	CH_2CH_3
A-40	(R) $CH(CH_3)$-$CH(CH_3)_2$	H
A-41	(R) $CH(CH_3)$-$CH(CH_3)_2$	CH_3
A-42	(R) $CH(CH_3)$-$CH(CH_3)_2$	CH_2CH_3
A-43	(±) $CH(CH_3)$-$C(CH_3)_3$	H
A-44	(±) $CH(CH_3)$-$C(CH_3)_3$	CH_3
A-45	(±) $CH(CH_3)$-$C(CH_3)_3$	CH_2CH_3
A-46	(S) $CH(CH_3)$-$C(CH_3)_3$	H
A-47	(S) $CH(CH_3)$-$C(CH_3)_3$	CH_3
A-48	(S) $CH(CH_3)$-$C(CH_3)_3$	CH_2CH_3
A-49	(R) $CH(CH_3)$-$C(CH_3)_3$	H
A-50	(R) $CH(CH_3)$-$C(CH_3)_3$	CH_3
A-51	(R) $CH(CH_3)$-$C(CH_3)_3$	CH_2CH_3
A-52	(±) $CH(CH_3)$-CF_3	H

No.	R^1	R^2
A-53	(±) $CH(CH_3)$-CF_3	CH_3
A-54	(±) $CH(CH_3)$-CF_3	CH_2CH_3
A-55	(S) $CH(CH_3)$-CF_3	H
A-56	(S) $CH(CH_3)$-CF_3	CH_3
A-57	(S) $CH(CH_3)$-CF_3	CH_2CH_3
A-58	(R) $CH(CH_3)$-CF_3	H
A-59	(R) $CH(CH_3)$-CF_3	CH_3
A-60	(R) $CH(CH_3)$-CF_3	CH_2CH_3
A-61	(±) $CH(CH_3)$-CCl_3	H
A-62	(±) $CH(CH_3)$-CCl_3	CH_3
A-63	(±) $CH(CH_3)$-CCl_3	CH_2CH_3
A-64	(S) $CH(CH_3)$-CCl_3	H
A-65	(S) $CH(CH_3)$-CCl_3	CH_3
A-66	(S) $CH(CH_3)$-CCl_3	CH_2CH_3
A-67	(R) $CH(CH_3)$-CCl_3	H
A-68	(R) $CH(CH_3)$-CCl_3	CH_3
A-69	(R) $CH(CH_3)$-CCl_3	CH_2CH_3
A-70	$CH_2CF_2CF_3$	H
A-71	$CH_2CF_2CF_3$	CH_3
A-72	$CH_2CF_2CF_3$	CH_2CH_3
A-73	$CH_2(CF_2)_2CF_3$	H
A-74	$CH_2(CF_2)_2CF_3$	CH_3
A-75	$CH_2(CF_2)_2CF_3$	CH_2CH_3
A-76	$CH_2C(CH_3)=CH_2$	H
A-77	$CH_2C(CH_3)=CH_2$	CH_3
A-78	$CH_2C(CH_3)=CH_2$	CH_2CH_3
A-79	$CH_2CH=CH_2$	H
A-80	$CH_2CH=CH_2$	CH_3
A-81	$CH_2CH=CH_2$	CH_2CH_3
A-82	$CH(CH_3)CH=CH_2$	H
A-83	$CH(CH_3)CH=CH_2$	CH_3
A-84	$CH(CH_3)CH=CH_2$	CH_2CH_3

No.	R^1	R^2
A-85	$CH(CH_3)C(CH_3)=CH_2$	H
A-86	$CH(CH_3)C(CH_3)=CH_2$	CH_3
A-87	$CH(CH_3)C(CH_3)=CH_2$	CH_2CH_3
A-88	CH_2-C≡CH	H
A-89	CH_2-C≡CH	CH_3
A-90	CH_2-C≡CH	CH_2CH_3
A-91	cyclopentyl	H
A-92	cyclopentyl	CH_3
A-93	cyclopentyl	CH_2CH_3
A-94	cyclohexyl	H
A-95	cyclohexyl	CH_3
A-96	cyclohexyl	CH_2CH_3
A-97	CH_2-C_6H_5	H
A-98	CH_2-C_6H_5	CH_3
A-99	CH_2-C_6H_5	CH_2CH_3
A-100	$-(CH_2)_2CH=CHCH_2-$	
A-101	$-(CH_2)_2C(CH_3)=CHCH_2-$	
A-102	$-CH(CH_3)CH_2-CH=CHCH_2-$	
A-103	$-(CH_2)_2CH(CH_3)(CH_2)_2-$	
A-104	$-(CH_2)_3CHFCH_2-$	
A-105	$-(CH_2)_2CHF(CH_2)_2-$	
A-106	$-CH_2CHF(CH_2)_3-$	
A-107	$-(CH_2)_2CH(CF_3)(CH_2)_2-$	
A-108	$-(CH_2)_2O(CH_2)_2-$	
A-109	$-(CH_2)_2S(CH_2)_2-$	
A-110	$-(CH_2)_5-$	
A-111	$-(CH_2)_4-$	
A-112	$-CH_2CH=CHCH_2-$	
A-113	$-CH(CH_3)(CH_2)_3-$	
A-114	$-CH_2CH(CH_3)(CH_2)_2-$	
A-115	$-CH(CH_3)-(CH_2)_2-CH(CH_3)-$	
A-116	$-CH(CH_3)-(CH_2)_4-$	

No.	R^1	R^2
A-117	$-CH_2-CH(CH_3)-(CH_2)_3-$	
A-118	$-(CH_2)-CH(CH_3)-CH_2-CH(CH_3)-CH_2-$	
A-119	$-CH(CH_2CH_3)-(CH_2)_4-$	
A-120	$-(CH_2)_2-CHOH-(CH_2)_2-$	
A-121	$-(CH_2)_6-$	
A-122	$-CH(CH_3)-(CH_2)_5-$	
A-123	$-(CH_2)_2-N(CH_3)-(CH_2)_2-$	
A-124	-N=CH-CH=CH-	
A-125	$-N=C(CH_3)-CH=C(CH_3)-$	
A-126	$-N=C(CF_3)-CH=C(CF_3)-$	

The compounds I are suitable as fungicides. They are distinguished by an outstanding effectiveness against a broad spectrum of phytopathogenic fungi, especially from the classes of the *Ascomycetes, Deuteromycetes, Oomycetes* and *Basidiomycetes*. Some are systemically effective and they can be used in plant protection as foliar and soil fungicides.

They are particularly important in the control of a multitude of fungi on various cultivated plants, such as wheat, rye, barley, oats, rice, maize, grass, bananas, cotton, soya, coffee, sugar cane, vines, fruits and ornamental plants, and vegetables, such as cucumbers, beans, tomatoes, potatoes and cucurbits, and on the seeds of these plants.

They are especially suitable for controlling the following plant diseases:

- *Alternaria* species on fruit and vegetables,
- *Bipolaris* and *Drechslera* species on cereals, rice and lawns,
- *Blumeria graminis* (powdery mildew) on cereals,
- *Botrytis cinerea* (gray mold) on strawberries, vegetables, ornamental plants and grapevines,
- *Erysiphe cichoracearum* and *Sphaerotheca fuliginea* on cucurbits,
- *Fusarium* and *Verticillium* species on various plants,
- *Mycosphaerella* species on cereals, bananas and peanuts,
- *Phytophthora infestans* on potatoes and tomatoes,
- *Plasmopara viticola* on grapevines,

- *Podosphaera leucotricha* on apples,
- *Pseudocercosporella herpotrichoides* on wheat and barley,
- *Pseudoperonospora* species on hops and cucumbers,
- *Puccinia* species on cereals,
- *Pyricularia oryzae* on rice,
- *Rhizoctonia* species on cotton, rice and lawns,
- *Septoria tritici* and *Stagonospora nodorum* on wheat,
- *Uncinula necator* on grapevines,
- *Ustilago* species on cereals and sugar cane, and
- *Venturia* species (scab) on apples and pears.

The compounds I are also suitable for controlling harmful fungi, such as *Paecilomyces variotii*, in the protection of materials (e.g. wood, paper, paint dispersions, fibers or fabrics) and in the protection of stored products.

The compounds I are employed by treating the fungi or the plants, seeds, materials or soil to be protected from fungal attack with a fungicidally effective amount of the active compounds. The application can be carried out both before and after the infection of the materials, plants or seeds by the fungi.

The fungicidal compositions generally comprise between 0.1 and 95%, preferably between 0.5 and 90%, by weight of active compound.

When employed in plant protection, the amounts applied are, depending on the kind of effect desired, between 0.01 and 2.0 kg of active compound per ha.

In seed treatment, amounts of active compound of 1 to 1000 g/100 kg of seed, preferably 1 to 200 g/100 kg, in particular 5 to 100 g/100 kg are generally used.

When used in the protection of materials or stored products, the amount of active compound applied depends on the kind of application area and on the effect desired. Amounts customarily applied in the protection of materials are, for example, 0.001 g to 2 kg, preferably 0.005 g to 1 kg, of active compound per cubic meter of treated material.

The compounds I can be converted into the customary formulations, for example solutions, emulsions, suspensions, dusts, powders, pastes and granules. The application form depends on the particular purpose; in each case, it should ensure a fine and uniform distribution of the compound according to the invention.

The formulations are prepared in a known manner, for example by extending the active compound with solvents and/or carriers, if desired using emulsifiers and dispersants. Solvents/auxiliaries which are suitable are essentially:

- water, aromatic solvents (for example Solvesso products, xylene), paraffins (for example mineral oil fractions), alcohols (for example methanol, butanol, pentanol, benzyl alcohol), ketones (for example cyclohexanone, gamma-butyrolactone), pyrrolidones (NMP, NOP), acetates (glycol diacetate), glycols, fatty acid dimethylamides, fatty acids and fatty acid esters. In principle, solvent mixtures may also be used,
- carriers such as ground natural minerals (for example kaolins, clays, talc, chalk) and ground synthetic minerals (for example highly disperse silica, silicates); emulsifiers such as nonionic and anionic emulsifiers (for example polyoxyethylene fatty alcohol ethers, alkylsulfonates and arylsulfonates) and dispersants such as lignosulfite waste liquors and methylcellulose.

Suitable surfactants are alkali metal, alkaline earth metal and ammonium salts of lignosulfonic acid, naphthalenesulfonic acid, phenolsulfonic acid, dibutylnaphthalenesulfonic acid, alkylarylsulfonates, alkyl sulfates, alkylsulfonates, fatty alcohol sulfates, fatty acids and sulfated fatty alcohol glycol ethers, furthermore condensates of sulfonated naphthalene and naphthalene derivatives with formaldehyde, condensates of naphthalene or of naphthalenesulfonic acid with phenol and formaldehyde, polyoxyethylene octylphenol ether, ethoxylated isooctylphenol, octylphenol, nonylphenol, alkylphenol polyglycol ethers, tributylphenyl polyglycol ether, tristearylphenyl polyglycol ether, alkylaryl polyether alcohols, alcohol and fatty alcohol/ethylene oxide condensates, ethoxylated castor oil, polyoxyethylene alkyl ethers, ethoxylated polyoxypropylene, lauryl alcohol polyglycol ether acetal, sorbitol esters, lignosulfite waste liquors and methylcellulose.

Suitable for the preparation of directly sprayable solutions, emulsions, pastes or oil dispersions are mineral oil fractions of medium to high boiling point, such as kerosene or diesel oil, furthermore coal tar oils and oils of vegetable or animal origin, aliphatic, cyclic and aromatic hydrocarbons, for example toluene, xylene, paraffin, tetrahydronaphthalene, alkylated naphthalenes or their derivatives, methanol, ethanol, propanol, butanol, cyclohexanol, cyclohexanone, isophorone, strongly polar solvents, for example dimethyl sulfoxide, N-methylpyrrolidone and water.

Powders, materials for spreading and dustable products can be prepared by mixing or concomitantly grinding the active substances with a solid carrier.

Granules, for example coated granules, impregnated granules and homogeneous granules, can be prepared by binding the active compounds to solid carriers. Examples of solid carriers are mineral earths such as silica gels, silicates, talc, kaolin, attaclay, limestone, lime, chalk, bole, loess, clay, dolomite, diatomaceous earth, calcium sulfate, magnesium sulfate, magnesium oxide, ground synthetic materials, fertilizers, such as, for example, ammonium sulfate, ammonium phosphate, ammonium nitrate, ureas, and products of vegetable origin, such as cereal meal, tree bark meal, wood meal and nutshell meal, cellulose powders and other solid carriers.

In general, the formulations comprise from 0.01 to 95% by weight, preferably from 0.1 to 90% by weight, of the active compound. The active compounds are employed in a purity of from 90% to 100%, preferably 95% to 100% (according to NMR spectrum).

The following are examples of formulations: 1. Products for dilution with water

A Water-soluble concentrates (SL)

10 parts by weight of a compound according to the invention are dissolved in water or in a water-soluble solvent. As an alternative, wetters or other auxiliaries are added. The active compound dissolves upon dilution with water.

B Dispersible concentrates (DC)

20 parts by weight of a compound according to the invention are dissolved in

cyclohexanone with addition of a dispersant, for example polyvinylpyrrolidone. Dilution with water gives a dispersion.

C Emulsifiable concentrates (EC)

15 parts by weight of a compound according to the invention are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5%). Dilution with water gives an emulsion.

D Emulsions (EW, EO)

40 parts by weight of a compound according to the invention are dissolved in xylene with addition of calcium dodecylbenzenesulfonate and castor oil ethoxylate (in each case 5%). This mixture is introduced into water by means of an emulsifying machine (Ultraturrax) and made into a homogeneous emulsion. Dilution with water gives an emulsion.

E Suspensions (SC, OD)

In an agitated ball mill, 20 parts by weight of a compound according to the invention are comminuted with addition of dispersants, wetters and water or an organic solvent to give a fine active compound suspension. Dilution with water gives a stable suspension of the active compound.

F Water-dispersible granules and water-soluble granules (WG, SG)

50 parts by weight of a compound according to the invention are ground finely with addition of dispersants and wetters and made into water-dispersible or water-soluble granules by means of technical appliances (for example extrusion, spray tower, fluidized bed). Dilution with water gives a stable dispersion or solution of the active compound.

G Water-dispersible powders and water-soluble powders (WP, SP)

75 parts by weight of a compound according to the invention are ground in a rotor–stator mill with addition of dispersants, wetters and silica gel. Dilution with water gives a stable dispersion or solution of the active compound.

2. Products to be applied undiluted

H Dustable powders (DP)

5 parts by weight of a compound according to the invention are ground finely and mixed intimately with 95% of finely divided kaolin. This gives a dustable product.

I Granules (GR, FG, GG, MG)

0.5 part by weight of a compound according to the invention is ground finely and associated with 95.5% carriers. Current methods are extrusion, spray-drying or the fluidized bed. This gives granules to be applied undiluted.

J ULV solutions (UL)

10 parts by weight of a compound according to the invention are dissolved in an organic solvent, for example xylene. This gives a product to be applied undiluted.

The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, for example in the form of directly sprayable solutions, powders, suspensions or dispersions, emulsions, oil dispersions, pastes, dustable products, materials for spreading, or granules, by means of spraying, atomizing, dusting, spreading or pouring. The use forms depend entirely on the intended uses; the intention is to ensure in each case the finest possible distribution of the active compounds according to the invention.

Aqueous use forms can be prepared from emulsion concentrates, pastes or wettable powders (sprayable powders, oil dispersions) by adding water. To prepare emulsions, pastes or oil dispersions, the substances, as such or dissolved in an oil or solvent, can be homogenized in water by means of a wetter, tackifier, dispersant or emulsifier. Alternatively, it is possible to prepare concentrates composed of active substance wetter, tackifier, dispersant or emulsifier and, if appropriate, solvent or oil, and such concentrates are suitable for dilution with water.

The active compound concentrations in the ready-to-use preparations can be varied within relatively wide ranges. In general, they are from 0.0001 to 10%, preferably from 0.01 to 1%.

The active compounds may also be used successfully in the ultra-low-volume process (ULV), by which it is possible to apply formulations comprising over 95% by weight of active compound, or even to apply the active compound without additives.

Various types of oils, wetters, adjuvants, herbicides, fungicides, other pesticides, or bactericides may be added to the active compounds, if appropriate not until immediately prior to use (tank mix). These agents can be admixed with the agents according to the invention in a weight ratio of 1:10 to 10:1.

The compositions according to the invention can, in the use form as fungicides, also be present together with other active compounds, e.g. with herbicides, insecticides, growth regulators, fungicides or else with fertilizers. Mixing the compounds I or the compositions comprising them in the application form as fungicides with other fungicides results in many cases in an expansion of the fungicidal spectrum of activity being obtained.

The following list of fungicides, in conjunction with which the compounds according to the invention can be used, is intended to illustrate the possible combinations but does not limit them:

- acylalanines, such as benalaxyl, metalaxyl, ofurace or oxadixyl,
- amine derivatives, such as aldimorph, dodine, dodemorph, fenpropimorph, fenpropidin, guazatine, iminoctadine, spiroxamine or tridemorph,
- anilinopyrimidines, such as pyrimethanil, mepanipyrim or cyprodinyl,
- antibiotics, such as cycloheximide, griseofulvin, kasugamycin, natamycin, polyoxin or streptomycin,
- azoles, such as bitertanol, bromoconazole, cyproconazole, difenoconazole, dinitroconazole, enilconazole, epoxiconazole, fenbuconazole, fluquinconazole, flusilazole, flutriatol, hexaconazole, imazalil, metconazole, myclobutanil, penconazole, propiconazole, prochloraz, prothioconazole, tebuconazole, triadimefon, triadimenol, triflumizole or triticonazole,
- dicarboximides, such as iprodione, myclozolin, procymidone or vinclozolin,
- dithiocarbamates, such as ferbam, nabam, maneb, mancozeb, metam, metiram, propineb, polycarbamate, thiram, ziram or zineb,
- heterocyclic compounds, such as anilazine, benomyl, boscalid, carbendazim, carboxin, oxycarboxin, cyazofamid, dazomet, dithianon, famoxadone, fenamidone, fenarimol, fuberidazole, flutolanil, furametpyr, isoprothiolane, mepronil, nuarimol, probenazole, proquinazid, pyrifenox, pyroquilon, quinoxyfen, silthiofam, thiabendazole, thifluzamide, thiophanate-methyl, tiadinil, tricyclazole or triforine,

- copper fungicides, such as Bordeaux mixture, copper acetate, copper oxychloride or basic copper sulfate,
- nitrophenyl derivatives, such as binapacryl, dinocap, dinobuton or nitrophthal-isopropyl,
- phenylpyrroles, such as fenpiclonil or fludioxonil,
- sulfur,
- other fungicides, such as acibenzolar-S-methyl, benthiavalicarb, carpropamid, chlorothalonil, cyflufenamid, cymoxanil, dazomet, diclomezine, diclocymet, diethofencarb, edifenphos, ethaboxam, fenhexamid, fentin-acetate, fenoxanil, ferimzone, fluazinam, fosetyl, fosetyl-aluminum, iprovalicarb, hexachlorobenzene, metrafenone, pencycuron, propamocarb, phthalide, tolclofos-methyl, quintozene or zoxamide,
- strobilurins, such as azoxystrobin, dimoxystrobin, fluoxastrobin, kresoxim-methyl, metominostrobin, orysastrobin, picoxystrobin, pyraclostrobin or trifloxystrobin,
- sulfenic acid derivatives, such as captafol, captan, dichlofluanid, folpet or tolylfluanid,
- cinnamides and analogous compounds, such as dimethomorph, flumetover or flumorph.

Synthesis examples

The procedures described in the synthesis examples below were used to prepare further compounds I by appropriate modification of the starting compounds. The compounds thus obtained are listed in the tables below, together with physical data.

Example 1: Preparation of diethyl 2-chloro-5-fluorophenylmalonate

At about 60°C, diethyl malonate (0.49 mol) was added, over a period of 2 hours, to a suspension of sodium hydride (0.51 mol) in 140 ml of 1,4-dioxane. After a further 10 min of stirring, 0.05 mol of CuBr was added. After 15 min, 0.25 mol of 2-chloro-5-fluorobromobenzene in 10 ml of dioxane was added. The reaction mixture was maintained at 100°C for about 14 hours and, at about 15°C, 35 ml of 12 N hydrochloric acid were then added slowly. The precipitate was filtered off and the filtrate was extracted with diethyl ether. After phase separation, the organic phase was dried and then freed from the solvent. 42 g of the title compound remained.

Example 2: Preparation of 5,7-dihydroxy-6-(2-chloro-5-fluorophenylphenyl)-[1,2,4]-triazolo[1,5-a]-pyrimidine

A mixture of 12 g of 3-amino-1,2,4-triazole, 0.17 mol of the ester from example 1 and 50 ml of tributylamine was stirred at 180°C for about 6 hours. At about 70°C, a solution of 21 g of NaOH in 200 ml of water was added, and the mixture was stirred for another 30 min. The organic phase was removed and the aqueous phase was extracted with diethyl ether. After acidification with conc. hydrochloric acid, the product precipitated from the aqueous phase. Filtration gave 33 g of the title compound.

Example 3: Preparation of
5,7-dichloro-6-(2-chloro-5-fluorophenyl)-[1,2,4]-triazolo[1,5-a]-pyrimidine

A mixture of 30 g of the triazolopyrimidine from example 2 and 50 ml of $POCl_3$ was heated under reflux for 8 hours; during this time, some $POCl_3$ distilled off. The residue was poured into a mixture of CH_2Cl_2 and water and the organic phase was separated off, washed and dried and then freed from the solvent. This gave 27 g of the title compound of m.p. 137°C.

Example 4: Preparation of 5-chloro-6-(2-chloro-5-fluorophenyl)-7-but-2-ylamino-[1,2,4]-triazolo[1,5-a]pyrimidine [I-3]

With stirring, a solution of 1.5 mmol of 2-butylamine and 1.5 mmol of triethylamine in 10 ml of dichloromethane was added to a solution of 1.5 mmol of the product from Ex. 3 in 10 ml of dichloromethane. The reaction mixture was stirred at 20-25°C for about 16 hours and then washed with dil. hydrochloric acid. The organic phase was removed, dried and freed from the solvent. Chromatography on silica gel gave 35 mg of the title compound of m.p. 171°C.

Table I – Compounds of the formula I

No.	R^1	R^2	L^1	L^2	X	Phys. data (m.p. [°C]; HPLC/MS [R_t; m/z])
I-1	$CH_2C(CH_3)=CH_2$	CH_2CH_3	F	H	Cl	133
I-2	$-(CH_2)_2CH(CH_3)(CH_2)_2-$		F	H	Cl	188
I-3	(±) $CH(CH_3)-CH_2CH_3$	H	F	H	Cl	171
I-4	(S) $CH(CH_3)-CH_2CH_3$	H	F	H	Cl	168
I-5	(R) $CH(CH_3)-CH_2CH_3$	H	F	H	Cl	168
I-6	(±) $CH(CH_3)-CH(CH_3)_2$	H	F	H	Cl	111
I-7	(S) $CH(CH_3)-CH(CH_3)_2$	H	F	H	Cl	109

No.	R^1	R^2	L^1	L^2	X	Phys. data (m.p. [°C]; HPLC/MS [R_t; m/z])
I-8	(R) $CH(CH_3)$-$CH(CH_3)_2$	H	F	H	Cl	109
I-9	(±) $CH(CH_3)$-$C(CH_3)_3$	H	F	H	Cl	178
I-10	(S) $CH(CH_3)$-$C(CH_3)_3$	H	F	H	Cl	173
I-11	(R) $CH(CH_3)$-$C(CH_3)_3$	H	F	H	Cl	173
I-12	(±) $CH(CH_3)$-CF_3	H	F	H	Cl	155
I-13	(S) $CH(CH_3)$-CF_3	H	F	H	Cl	157
I-14	(R) $CH(CH_3)$-CF_3	H	F	H	Cl	157
I-15	CH_2CF_3	H	F	H	Cl	175
I-16	-$(CH_2)_2$-$CH(CH_3)$-$(CH_2)_2$-		F	OCH_3	Cl	Harz
I-17	CH_2-$C(=CH_2)$-CH_3	CH_2CH_3	F	OCH_3	Cl	3.94 min; 410 $(M+H)^+$
I-18	(±) $CH(CH_3)C(CH_3)_3$	H	F	OCH_3	Cl	3.91 min; 412 $(M+H)^+$
I-19	(±) $CH(CH_3)CH(CH_3)_2$	H	F	OCH_3	Cl	3.71 min; 398 $(M+H)^+$
I-20	(±) $CH(CH_3)CH_2$-CH_3	H	F	OCH_3	Cl	3.53 min; 384 $(M+H)^+$
I-21	-$CH(CH_3)$-$(CH_2)_3$-		F	OCH_3	Cl	3.62 min; 396 $(M+H)^+$
I-22	-$CH(CH_3)$-$(CH_2)_4$-		F	OCH_3	Cl	3.88 min; 410 $(M+H)^+$
I-23	-CH_2-$CH(CH_3)$-$(CH_2)_2$-		F	OCH_3	Cl	3.62 min; 396 $(M+H)^+$
I-24	(R) $CH(CH_3)$-$C(CH_3)_3$	H	F	OCH_3	Cl	3.91 min; 412 $(M+H)^+$
I-25	(R) $CH(CH_3)CH(CH_3)_2$	H	F	OCH_3	Cl	3.72 min; 398 $(M+H)^+$
I-26	(±) $CH(CH_3)$-CF_3	H	F	OCH_3	Cl	175-177
I-27	CH_2-CF_3	H	F	OCH_3	Cl	191-193
I-28	CH_2-CF_3	CH_3	F	OCH_3	Cl	3.50 min; 424 $(M+H)^+$
I-29	(S) $CH(CH_3)$-CF_3	H	F	OCH_3	Cl	108-110
I-30	$CH_2C(CH_3)=CH_2$	CH_2CH_3	Cl	H	Cl	128-130
I-31	-$(CH_2)_2CH(CH_3)(CH_2)_2$-		Cl	H	Cl	186-187
I-32	(±) $CH(CH_3)C(CH_3)_3$	H	Cl	H	Cl	157-158
I-33	(R)-$CH(CH_3)$-$C(CH_3)_3$	H	Cl	H	Cl	187-188
I-34	(±)-$CH(CH_3)CH(CH_3)_2$	H	Cl	H	Cl	142-144
I-35	(R)-$CH(CH_3)CH(CH_3)_2$	H	Cl	H	Cl	137-138
I-36	±)-$CH(CH_3)CH_2CH_3$	H	Cl	H	Cl	109-110
I-37	(R)-$CH(CH_3)CH_2CH_3$	H	Cl	H	Cl	106-107
I-38	(±)-$CH(CH_3)$-CF_3	H	Cl	H	Cl	180-181
I-39	(S)-$CH(CH_3)$-CF_3	H	Cl	H	Cl	130-131

No.	R^1	R^2	L^1	L^2	X	Phys. data (m.p. [°C]; HPLC/MS [R_t; m/z])
I-40	CH_2CF_3	H	Cl	H	Cl	185-190

HPLC/MS:

HPLC column: RP-18 (Chromolith Speed ROD, Merck KgaA, Germany); mobile phase: acetonitrile + 0.1% of trifluoroacetic acid (TFA)/water + 0.1% of TFA in gradients 5:95 - 95:5 (5 min)/40°C.

MS: Quadrupole Elektrospray Ionization, 80 V (positive mode)

Examples for the action against harmful fungi

The fungicidal action of the compounds of the formula I was demonstrated by the following tests:

The active compounds were prepared as a stock solution comprising 0.25% by weight of active compound in acetone or DMSO. 1% by weight of the emulsifier Uniperol® EL (wetting agent having emulsifying and dispersing action based on ethoxylated alkylphenols) was added to this solution, and the mixture was diluted with water to the desired concentration.

Use Example 1 - Activity against early blight of tomato caused by *Alternaria solani*

Leaves of potted plants of the cultivar "Goldene Prinzessin" were sprayed to run-off point with an aqueous suspension having the concentration of active compounds stated below. The next day, the leaves were infected with an aqueous spore suspension of *Alternaria solani* in 2 % biomalt solution having a density of 0.17 x 10^6 spores/ml. The plants were then placed in a water-vapor-saturated chamber at temperatures of between 20 and 22°C. After 5 days, the infection on the untreated, but infected control plants had developed to such an extent that the infection could be determined visually in %.

In this test, the plants which had been treated with 63 ppm of the compounds I-1, I-13, I-15, I-23 to I-35, I-38, or I-39 showed an infection of at most 20%, whereas the untreated plants were 80% infected.

Use example 2: Curative activity against brown rust of wheat caused by *Puccinia recondita*

Leaves of potted wheat seedlings of the cultivar "Kanzler" were inoculated with a spore suspension of brown rust (*Puccinia recondita*). The pots were then placed in a chamber with high atmospheric humidity (90 to 95%), at 20-22°C, for 24 hours. During this time, the spores germinated and the germinal tubes penetrated into the leaf tissue. The next day, the infected plants were sprayed to run-off point with an aqueous suspension having the concentration of active compound stated below. The suspension or emulsion was prepared as described above. After the spray coating had dried on, the test plants were cultivated in a greenhouse at temperatures of between 20 and 22°C and at a relative atmospheric humidity of 65 to 70% for 7 days. The extent of the development of the rust fungus on the leaves was then determined.

In this test, the plants which had been treated with 63 ppm of the compounds I-3, I-13, I-15, I-16, I-18 to I-21, I-23 to I-27, I-29, I-34 to I-39 or I-40 showed an infection of at most 20%, whereas the untreated plants were 85 to 90% infected.